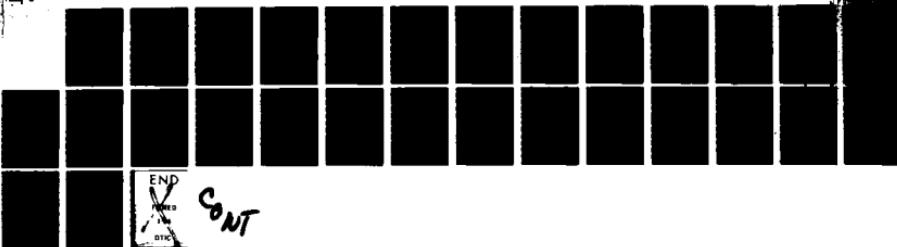
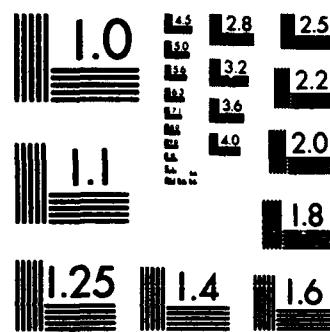


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21. ABSTRACT (Continue on reverse side if necessary and identify by block number) Amines in general and 3-aminopropyltriethoxysilane in particular were shown to improve the adhesion of a polyurethane to glass. At equivalent concentrations of amine in the solutions used to treat the glass the order of increase in the work of adhesion was 3-aminopropyltriethoxysilane >> 1,4-diaminobutane < p-phenylenediamine > piperazine >> aniline. The polyurethane was prepared from ARCO's hydroxyterminated polybutadiene, R-45HT, toluene diisocyanate, trimethylolpropane and N,N-bis(2-hydroxypropyl)aniline. The ratio ($-NCO/[total OH]$) was kept constant and equal to 1.0. The swelling		

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ratio, after curing, also remained constant. As the -NCO content compared to polymer-OH increased, the adhesion of the polyurethane to glass increased initially, passed through a maximum for prepolymers with 6% excess NCO, and then decreased again. Elongation at break behaved similarly but ultimate tensile strength reached a maximum and then stayed constant. The significance of these results is discussed. Adhesion of the polyurethane to chrome-plated steel did not show similar effects.

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Technical Report No. 29

FRACTURE MECHANICS APPLIED TO ELASTOMERIC COMPOSITES

by

F. Liang and P. Dreyfuss

Institute of Polymer Science
The University of Akron
Akron, Ohio 44325

December, 1983

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EFFECT OF AMINE SURFACE TREATMENT ON
THE ADHESION OF A POLYURETHANE TO THE SURFACE

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The University of Akron
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INTRODUCTION

This paper is a continuation of our investigation of the role amines play in adhesion. The overall investigation originated in repeated observations by ourselves and others that the presence of amine groups at an interface between a substrate and an adherend has a positive effect on the adhesion between the substrate and the adherend¹⁻⁴. In filled systems, mechanical properties compared to filled systems where the amines are absent are enhanced also. Previous work by Eckstein and Dreyfuss⁴⁻⁸ on peroxide cured bulk polybutadiene systems revealed both that the improvement in properties can be explained by the formation of chemical bonds through the amine group between the surface and the polymer and that the degree of improvement is related to the structure of the amine used.

In some applications of interest to us, notably solid fuel rocket propellants, polybutadiene is used as the soft segment of a polyurethane rather than as bulk polymer. Hence, our studies of the role of amines in adhesion have been extended to include systems with polyurethanes derived from functionalized liquid polybutadiene.

In polyurethane synthesis, amines are used both as chain extenders and as curing agents. The chemical reactions that occur and the products that form are well known⁹⁻¹¹. The questions that this study addressed were two. How does the structure of the amine used affect the adhesive properties of the resulting polyurethane and how can the observed effects be explained? This paper describes the synthesis and characterization of a new elastomeric polyurethane that shows remarkably high adhesion to glass and other substrates. A positive effect of amine surface treatment of the substrates on the adhesion of the polyurethane to the substrates is also reported. The results are interpreted in terms of the structure of the amines and of the polyurethane formed.

EXPERIMENTAL

Materials

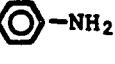
The materials used were: 1,4-diaminobutane, anhydrous piperazine, *p*-phenylenediamine, and 2-ethyl- 2-(hydroxymethyl)-1,3-propanediol from Aldrich Chemical Company, Inc.; aniline ("Baker Analyzed" Reagent) from J. T. Baker Chemical Co.; 3-aminopropyltriethoxysilane from Petrarch Systems Inc.; TDI (80/20 mixture of 2,4 and 2,6 isomers of toluene diisocyanates) from BASF Wyandotte Corporation; Isonol-100 (*N,N*-bis-(2-hydroxypropyl)aniline) from Upjohn Polymer Chemicals; and hydroxyterminated polybutadiene resin (R-45HT) from ARCO Chemical Co. ARCO lists the properties given in Table 1 for the latter resin.

Table 1. Properties of ARCO's R-45HT

Nonvolatile Material	wt%	99.9
Viscosity	poise 30°C	50
Hydroxyl Value	meq/gm	.083
Molecular Weight	No. Average	2800
Moisture	wt. %	0.05
Iodine Number		398
Trans-1,4 60%, Cis-1,4 20%, Vinyl-1,2 20%		

The amines were the same as those used in earlier studies⁴⁻⁸. Their properties are given in Table 2.

Table 2. List of Amines Used in Experiments

Amine	Structure	b.p. (°C)	m.p. (°C)	Symbol
1,4-diaminobutane	NH ₂ (CH ₂) ₄ NH ₂	159	27	AB
Piperazine	HN  NH	145	109	P
Aniline	 -NH ₂	184	-6.3	A
<i>p</i> -Phenylenediamine	H ₂ N  -NH ₂	267	140	PDA
3-Aminopropyltriethoxysilane	NH ₂ (CH ₂) ₃ Si(OEt) ₃	122/30mm		AS

Preparation of Polyurethane

The polyurethane was prepared from ARCO's hydroxyterminated polybutadiene (R-45HT), toluene diisocyanate (TDI), trimethylolpropane and N,N-bis(2-hydroxypropyl)aniline using a slightly modified two stage procedure from that described by ARCO^{1,2,13}. The ratio ([NCO]/[total OH] was kept constant and equal to 1.0 but the ratio [-NCO] to hydroxyl number of R-45HT was varied in some experiments. For adhesion studies, a 6% excess [-NCO] to hydroxyl number of R-45HT was used. The ratio of the substituted aniline to the triol was about 10 to 1 in most experiments. In one series, the latter ratio was varied.

The following equations were used to calculate the required amounts of diisocyanate and hydroxyl compounds.

a) Amount of the TDI for selected % free isocyanate in first stage:

$$\frac{\text{Wt of TDI}}{100\text{g polybd}} = \frac{100(\text{Equiv. Wt of TDI})}{(\text{Equiv. Wt of polybd})} \times$$

$$\frac{100(\text{Equiv Wt of NCO}) + (\text{Equiv Wt of polybd}) (\% \text{ Free NCO})}{100(\text{Equiv Wt of NCO}) - (\text{Equiv Wt of TDI}) (\% \text{ Free NCO})}$$

Where Equivalent Weight of polybd = 100/hydroxyl value

Equivalent Weight of NCO = 42

Equivalent Weight of TDI = 87

b) Amount of 2-ethyl-1,3-hexanediol (glycol) needed to react with prepolymer containing selected % free isocyanate from first stage:

$$\frac{\text{Weight of Glycol}}{100\text{g prepolymer}} = \frac{(\% \text{ Free NCO in prepolymer}) \times (\text{Equiv Wt of Glycol})}{42}$$

$$\text{Where Equiv Wt of Glycol} = \frac{1000 \times 56.1}{\text{hydroxyl number}}$$

$$= \frac{\text{Molecular Weight of Glycol}}{2}$$

In our experiments some of the calculated amount of diol was replaced by an equivalent amount (in terms of hydroxyl number) of triol. The total hydroxyl content of the mixture of triol and diol used in a particular experiment was equal to the hydroxyl content of the weight of glycol calculated as above for the selected % free isocyanate.

Surface Treatment of Substrates

Precleaned Opticlear soda lime microscope slides (75x25x1.06 mm) from KIMBLE were heated at 140°C for 1 hr., and kept in a dessicator over CaCl₂ until treated with the desired reagent. Amines used for surface treatment included p-phenylenediamine (PDA), 1,4-diaminobutane (AB), piperazine (P), aniline (A), and 3-aminopropyltriethoxysilane (AS). Glass slides were treated with amines at room temperature usually by immersing the slides for 5 min. in an amine-absolute ethanol solution. After removing the glass slides from the amine solution, the slides were dried in air and then heated for 30 min. at

60°C under vacuum before applying the elastomer layer. Pure ethanol treatment was carried out in the same manner. 3-Aminopropyltriethoxysilane was similarly applied except that a 50/50 mixture with water by volume was used instead of pure ethanol and after air drying the slides were heated at 100°C for 1 hr.

Small plates cut from Apollo mirror finish chrome ferro-type plates were similarly treated with amines. Before treatment the plates were cleaned with acetone and dried for 30 min. at 140°C.

Application of Elastomer Layer and Curing

For adhesion studies, appropriately treated substrates were placed in a Teflon coated compression mold and the prepolymer containing the glycol was poured on. The top plate of the mold was covered with a sheet of washed, dried and pressed cotton cloth. The sample was cured at 100°C for 4 hrs. in a heated press. Rubber sheets were cured in a vertical mold in a vacuum oven at 100°C for 5 hrs.

Measurement of Work of Adhesion (W_A)

180° peeling tests were carried out on strips of cloth backed elastomer layer after trimming them to a uniform width of 2 cm. on the substrate. The cloth-backed elastomer layer was peeled off the substrate at a constant rate of 0.5 cm/min. The work of adhesion per unit area of interface was calculated from the time average of the peel force P per unit width of the detaching layer: $W = 2P$.

Tensile Tests

Tensile tests were carried out at room temperature and a crosshead speed of 50 cm/min using dumbbell specimens. Breaking elongation was calculated from the ratio $(L_b - L_o)/L_o$, where L_o and L_b were the initial length and the length at break, respectively.

Swelling Ratio Measurements

Samples were cut from molded rod. The weight of a rod about 2.5 cm long and 0.6 cm in diameter was measured before, W_o , and after, W_f , immersion in dioxane solvent at room temperature for 70 hrs. The swelling ratio, calculated from the relationship $(W_f - W_o)/W_o$ remained constant throughout all experiments.

Differential Scanning Calorimetry

Differential scanning calorimetry was carried out with a du Pont 990 Thermal Analyzer and its accessories, using a normal scanning speed of 10°C/min and a sample weight of approximately 14 mg.

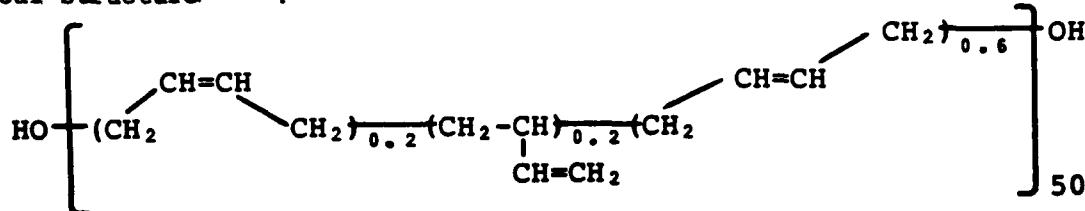
X-Ray Diffraction

Wide angle X-ray diffraction patterns were taken with a Phillips Universal Flat Plate Camera type PW 1030. The X-ray facility consisted of a Phillip's ultrastable generator model PW 1310/PW 1320.

RESULTS AND DISCUSSION

Effect of Free -NCO Content of Prepolymer on Properties of Polyurethane

According to ARCO, polybutadiene resin, R-45HT, has the following chemical structure¹²⁻¹³:



The hydroxyl functionality is slightly greater than 2.0. When excess isocyanate (TDI) is used in the preparation of a prepolymer in a two stage process, the hydroxyls are converted to urethane groups, $R'NCO'$, which can then react with the excess isocyanate to form allophanates, $R'NC-NR$.

Since 2-9% excess isocyanate was used to prepare the polymers in this study, the polymers undoubtedly contained some allophanate groups. The effect of excess -NCO content compared to hydroxyl number of the polybutadiene on tensile properties of the polyurethane are shown in Figure 1. As the -NCO content increased, the ultimate tensile strength, σ , passed through a maximum at about 6% excess -NCO and then stayed constant. As shown in Table 3 Shore A Hardness increased continuously with % free NCO content.

Table 3. Effect of Free NCO Content of Prepolymer on Swelling Ratio and Shore A Hardness of Polyurethane^a

Free NCO Content of Prepolymer	2%	3%	4%	6%	7%	9%
Swelling Ratio	--	4.02	4.05	4.08	4.13	3.94
Shore A Hardness	33	36	43	60	64	76

^aThe ratio of glycol to triol was about 10 to 1 in these experiments.

Polymerizations were completed by chain extension and crosslinking using N,N-bis-2-hydroxyaniline and trimethylolpropane, usually in a 10:1 ratio.

PROPERTIES OF POLYMER

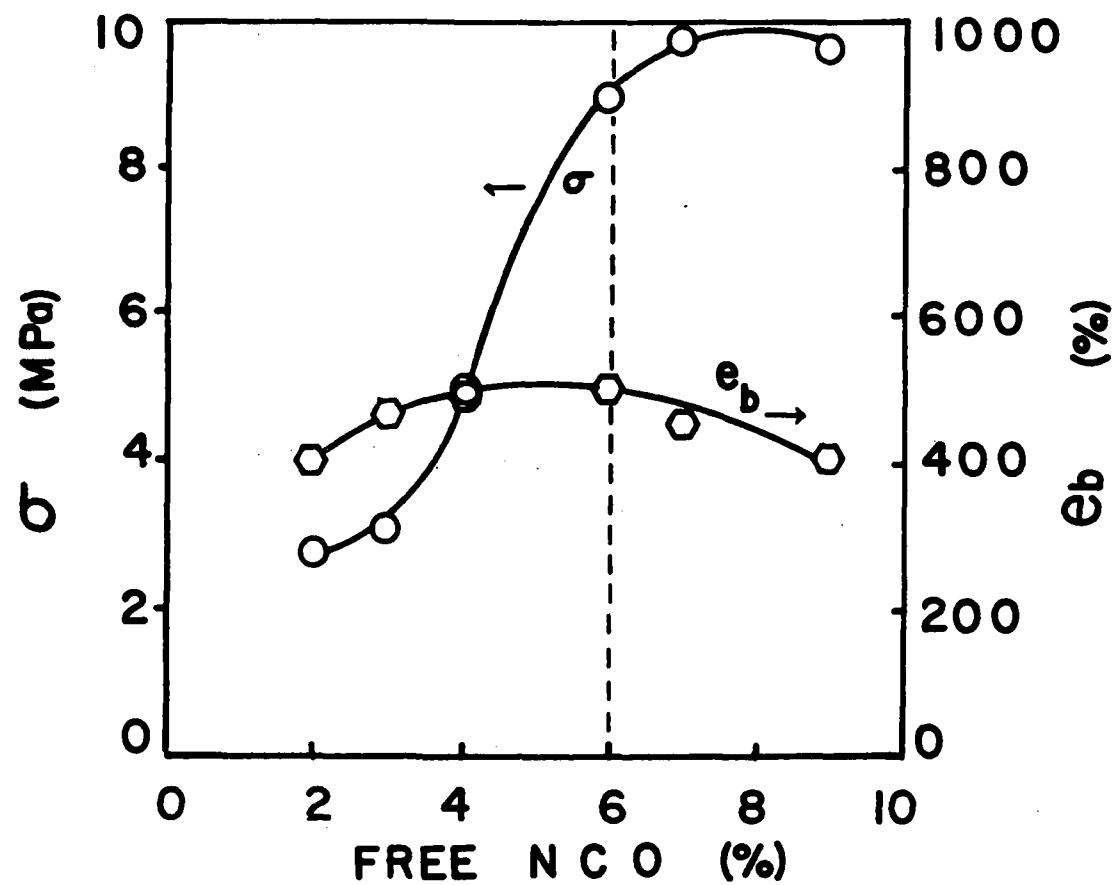


Fig. 1 Effect of free -NCO content of prepolymer on tensile strength (σ) and breaking elongation (e_b).

For these polymers, as shown in Table III, the swelling ratio remained constant. (The (total OH)/NCO ratio was constant and equal to 1.0.) As can be seen in Figure 1, elongation at break, e_b , passed through a maximum at about 6% excess -NCO and then decreased again.

Figure 2 shows the results of differential scanning calorimetry studies of these polymers. The glass transition temperature of the polybutadiene resin, R-45HT, is about -75°C. The glass transition temperature increases as the percentage of excess TDI used to make the polyurethane is increased. The behavior of T_g is similar to that of Shore A Hardness described above.

Wide angle X-ray photographs of a polyurethane whose prepolymer was prepared using 9% excess isocyanate groups did not show any evidence of crystallinity.

These effects occur because increasing the amount of TDI and chain extender with respect to the polybutadiene increases the relative concentration of urethane, allophanate, and other aromatic groups. This results in increased possibility for intermolecular hydrogen bonding, increased M_c , increased rigidity and increased elastomer strength.

Effect of Free -NCO Content of Prepolymer on Adhesion

The effect of free -NCO content of prepolymer on W_A to a glass substrate is shown in Figure 3. The results indicate that W_A increases initially as the -NCO content increases, reaches a maximum at ~6% free -NCO content and then decreases with further increases in -NCO content. As has already been mentioned above, increasing the free -NCO content of the prepolymer leads to an increase in the concentration of urethane groups in the elastomer backbone and results in increased intermolecular attractive forces in the elastomer. Reegen and Ilkka¹⁴ have made similar observations. They attributed the higher peel strength observed with increasing concentration of urethane groups to two factors: first, an increase in the true adhesion of the polyurethane and second, a more rigid and stiffer elastomer, which requires a greater force to bend it to an angle of 180°. In our experiments when the free -NCO content was over 6%, the rigidity of the elastomer increased so much that e_b and W_A decreased.

Effect of Water and Ethanol on Adhesion

A glass surface which has been exposed to the atmosphere is covered with a water film^{15,16}. When our polyurethane was applied to such a glass surface as shown in Figure 3 a much higher work of adhesion was obtained in comparison with a preheated glass surface. This can be explained as follows. The -NCO group can react with the water on the glass surface to form a primary amine, which on further reaction leads to urea linkages instead of the urethanes formed from alcohols. Urea groups are more polar than urethane groups and therefore promote higher adhesion than urethane groups.¹⁴

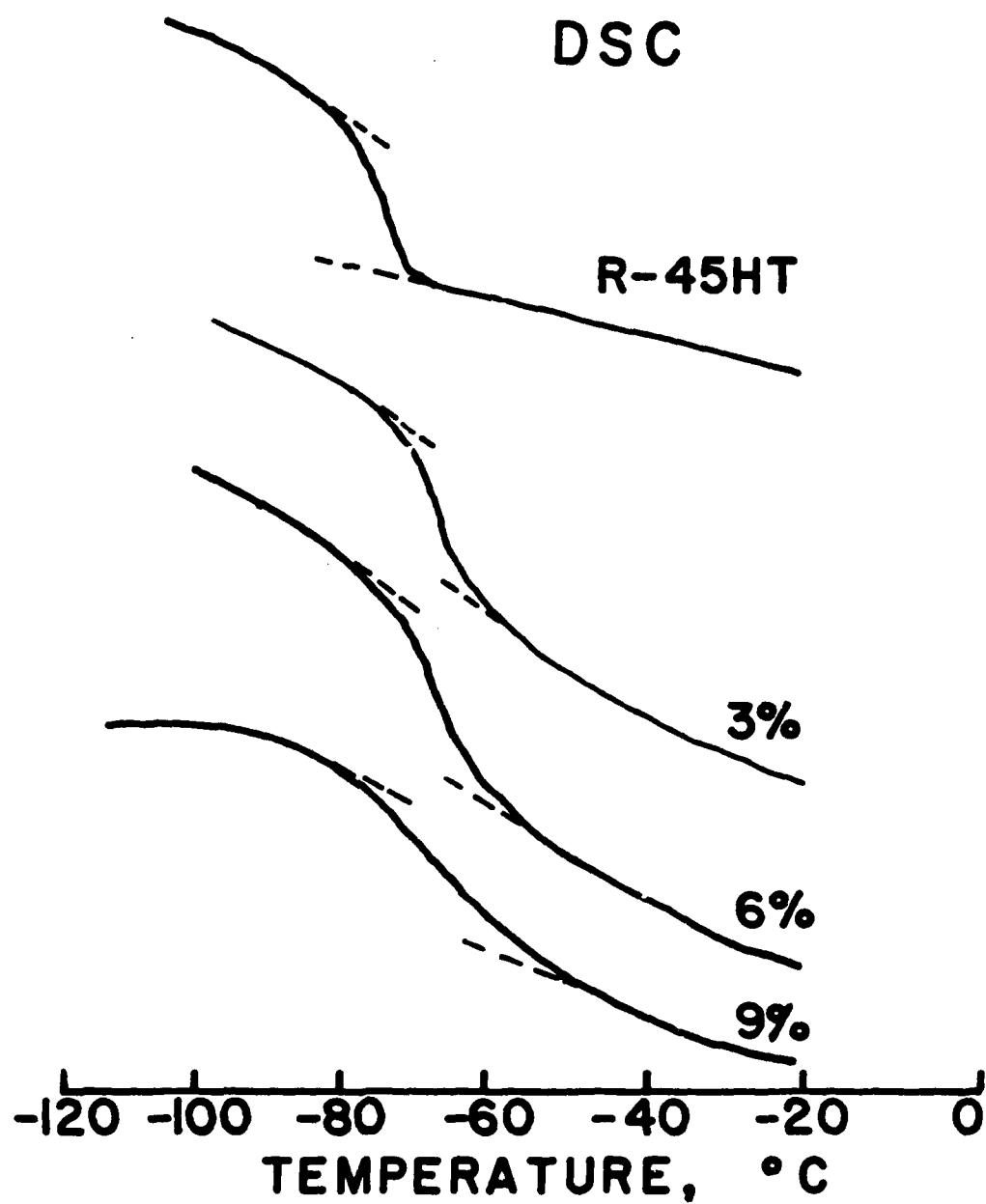


Fig. 2 Effect of concentration of excess TDI on glass transition temperature of resulting polyurethanes.

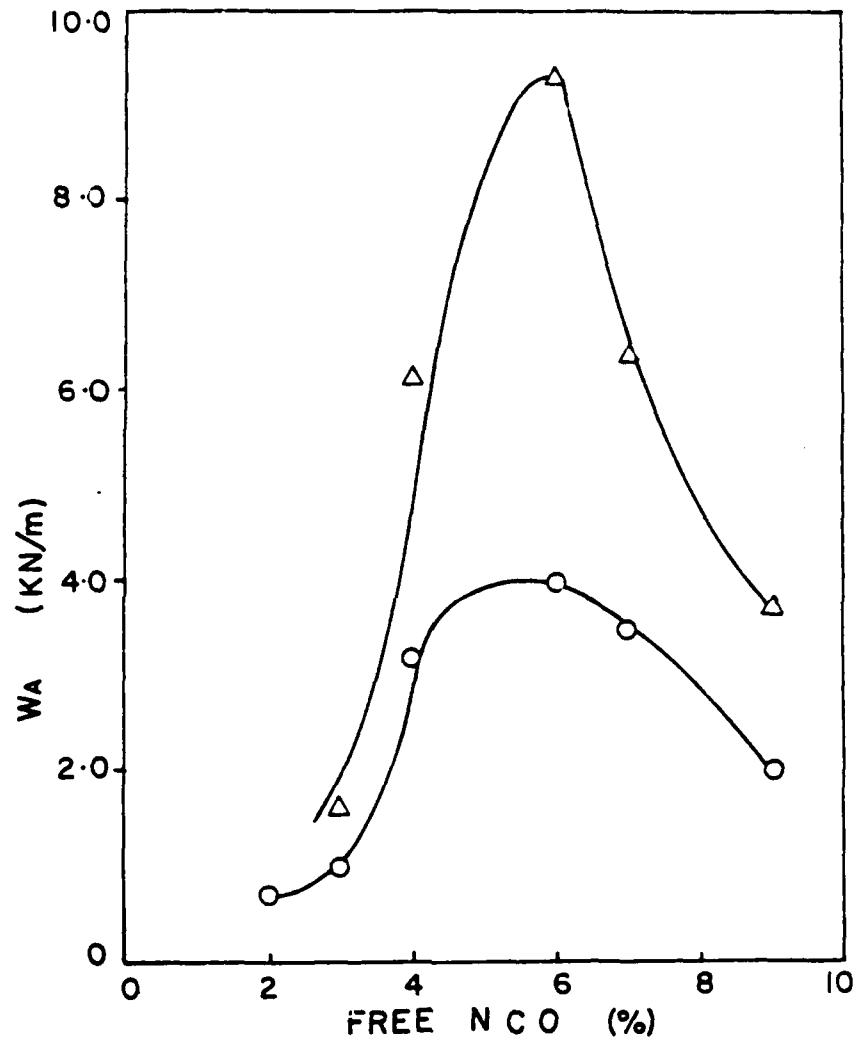
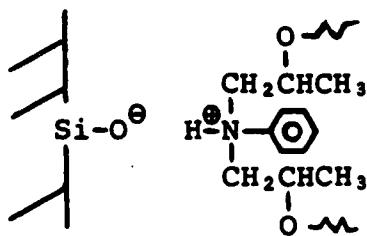


Fig. 3 Effect of free -NCO content of prepolymer on work of adhesion (W_A) of polyurethane to glass. Δ undried, \circ dried.

The formation of urea groups may not be the only explanation for the greatly enhanced adhesion of undried surfaces. The values of W_A observed for this polyurethane are substantially higher than those previously reported in the literature for other polyurethanes^{14,17}. We attribute the increased adhesion to the presence of tertiary amine groups from the N,N-bis(2-hydroxypropyl)aniline in the backbone of our polyurethane. These amine groups potentially can react with the acidic silanol groups present in the glass surface or perhaps even with surface moisture to form ionic bonds:



The presence of ionic groups in polyurethanes is known to drastically change the mechanical properties of polyurethanes¹⁸, but the remarkable effects on adhesion have not been reported previously. The presence of such ionic bonds is consistent with the fact that adhesion in these systems is markedly reduced by soaking a few days in water, which would solvate the ionic clusters¹⁸ and reduce their effectiveness in promoting adhesion. It is noteworthy that strong adhesive bonds reform on drying¹⁹.

Experiments intended to illustrate the effect of the concentration of tertiary amine groups on adhesion led to the remarkable changes in W_A shown in Figure 4. In this series of experiments the ratio of diol(tertiary amine) and triol was varied while a 6 percent excess isocyanate was maintained. Polymers with the greater percentage of diol were stronger and their swelling ratio was higher. Such systems have both an increased number of tertiary amine groups and are more chain extended than those prepared with the triol alone. Ahagon and Gent²⁰, among others, have shown that W_A decreases as the crosslink density of the polymer increases and the molecular weight between crosslinks decreases. Thus some of the increase in W_A with increased percent of diol is undoubtedly due to the decrease in crosslink density and polymer stiffness that accompanies the increase in diol. But the magnitude of the increase is greater than expected from this change alone. As stated above, we attribute the high strength of adhesion to the presence of ionic bonds. This interpretation is consistent with the observations of Kozakiewicz and Penczek²¹, who reported enhanced adhesion in systems shown to contain ionic bonds.

Preheated glass slides which had been immersed in absolute ethanol also led to a somewhat higher work of adhesion than untreated preheated slides, possibly due to an increased number of urethane groups at the interface.

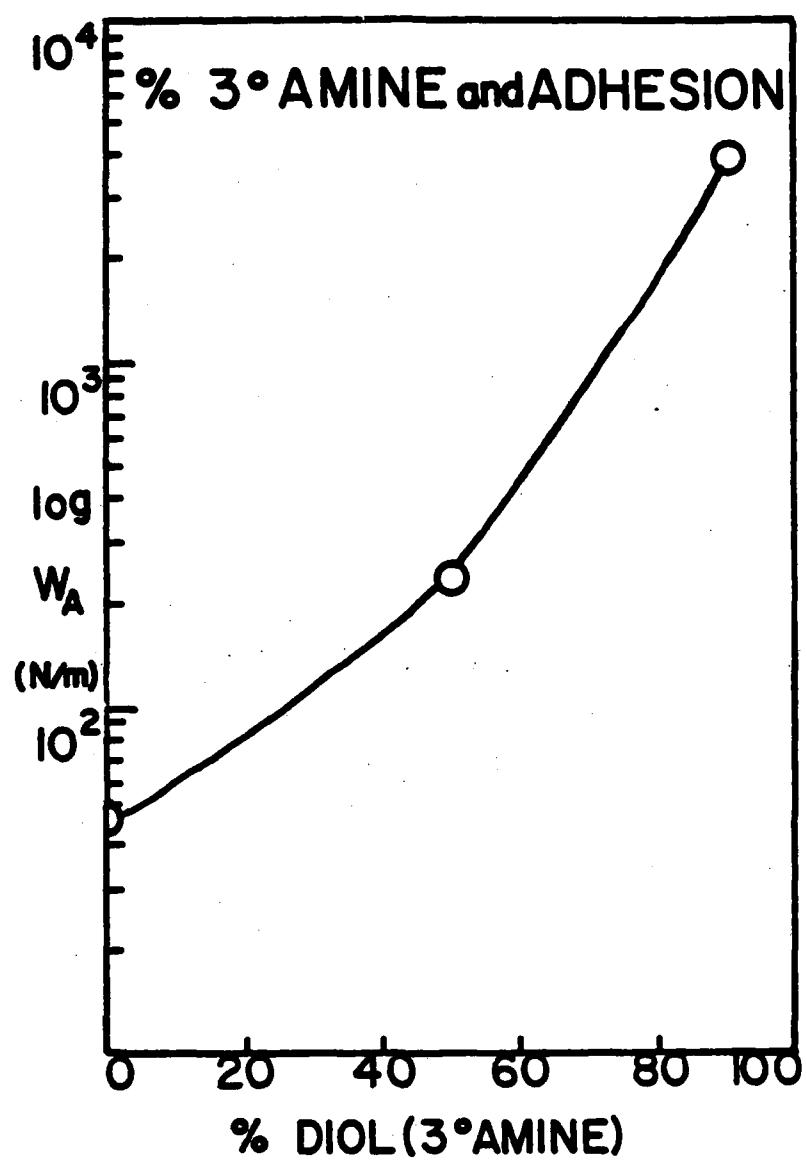
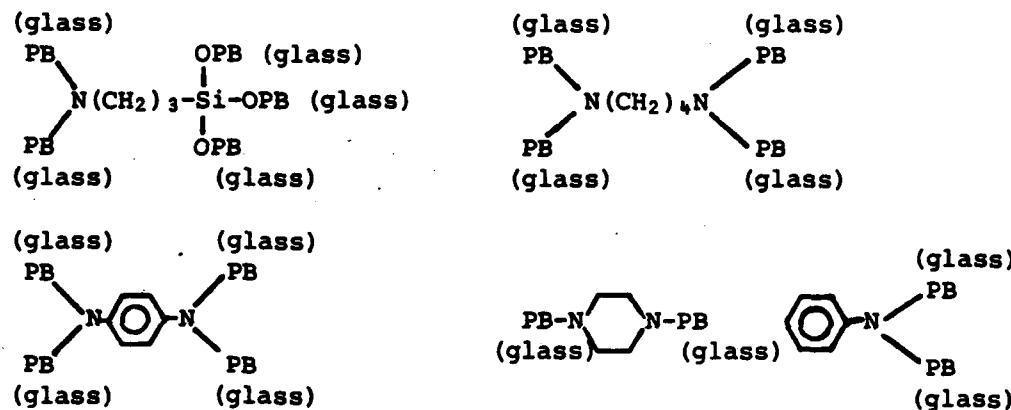


Fig. 4 Effect of concentration of diol (tertiary amine groups) on adhesion.

Effect of Amines on Adhesion

The values of the work of adhesion of our polyurethane to glass slides pretreated with different amine solutions are shown in Figures 5 and 6. The work of adhesion compared to untreated slides was increased in all cases except that of aniline. At equivalent concentration of amines, the order of enhancement in the work of adhesion was AS>>PDA~AB>P>>A. Cohesive failure of the adhesive bonds was observed for slides pretreated with AS. The results can be explained in terms of the different structures of the amines and the reactions that can occur with the amines. We conclude that just like in the work of Eckstein and Dreyfuss referred to above⁴⁻⁸, chemical bonds form from the surface through the amine to the substrate:



The degree of enhancement of adhesion is related to the number of bonds that can form between the surface and the adhesive. Aniline does not lead to reinforcement because it is monofunctional and the ring does not become part of the backbone.

The structures shown are intended to indicate that the amino groups can, in all cases, be bonded either to the glass or to the polybutadiene. The structures are not intended to suggest that bonding of the amine to the glass occurs only through the polybutadiene.

In the present case the chemical reactions occurring between the polybutadiene and the amines or glass are quite different from those described by Eckstein and Dreyfuss⁴⁻⁸, because in the present case no peroxide is present. All reactions occur among the functional endgroups. Bonding of the polybutadiene to the amines takes place as a result of the reaction of the isocyanate endgroups of the prepolymer with the amine to form a urea:



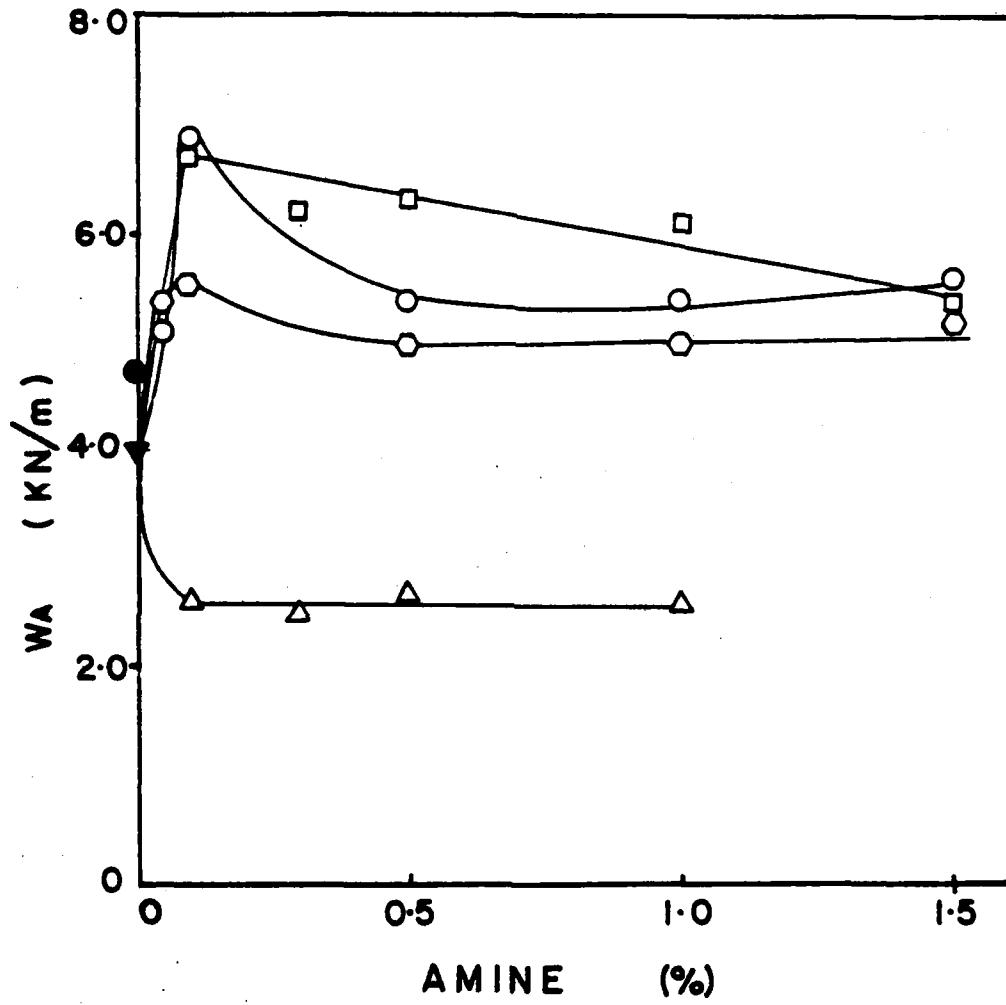


Fig. 5 Effect of concentration of amine on work of adhesion (W_A) of polyurethane to glass.
○ AB, □ PDA, ○ P, △ aniline, ● ethanol,
▼ dried and untreated.

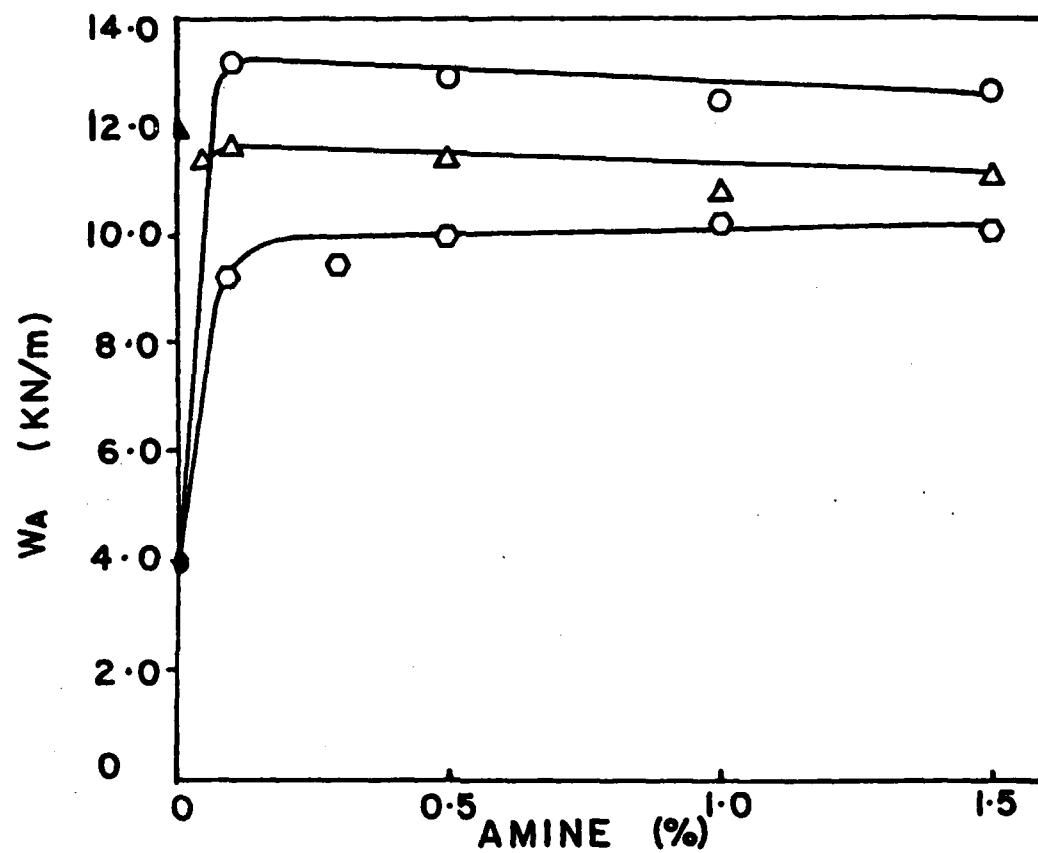
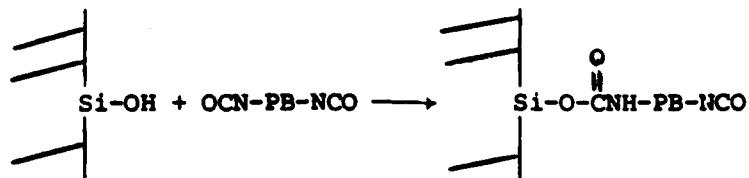
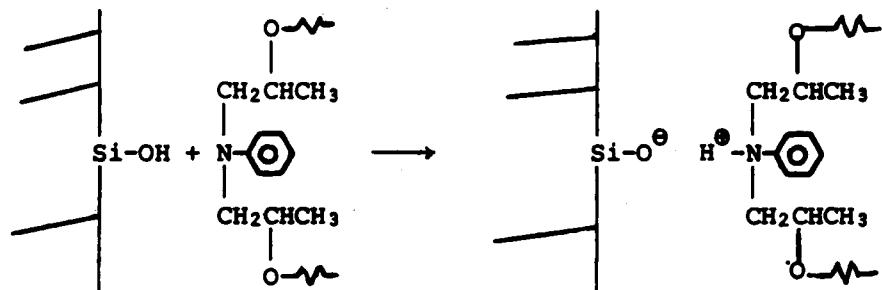


Fig. 6 Effect of concentration of AS on work of adhesion (W_A) of polyurethane to substrates.
○ glass treated with AS from 50/50 by volume
water/ethanol, △ chrome steel treated with
AB, ○ glass treated with AS from acetone,
△ chrome steel treated with absolute ethanol,
● dried and untreated glass.

Bonding of the polybutadiene to the glass may occur by reaction of the prepolymer with silanol groups in the glass surface:



With the present polyurethane, as stated above in the section on the effect of water on adhesion, ionic bonds form between the tertiary amine groups of the polybutadiene polyurethane and the silanol groups:



The reactions that occur between the glass and the amines are probably the same as those already described by Eckstein and Dreyfuss⁴⁻⁸. All of the amines can react with the silanol groups on the glass surface to form ionic bonds similar to those shown above for the tertiary amine. Reactions of 1,4-diaminobutane and 3-aminopropyltriethoxysilane are probably facilitated by prior formation of carbamates. In addition, covalent bonds of a presently undefined structure probably form between the glass and the amine.

Adhesion of Polyurethane to Chrome Steel

Metals have a higher surface energy than glass. After treatment with ethanol, W_A of our polyurethane to preheated and clean chrome steel surfaces was much higher than to preheated glass surfaces. Treating the surface of the steel with amines before applying the elastomer did not enhance adhesion. Dried and untreated surfaces had W_A of about 3 kN/m. The results are included in Figure 6. Some preliminary experiments have been carried out on chrome steel surfaces treated with AS. W_A is not significantly increased but the bonds that form are extremely stable in water. They can be soaked for a month with no apparent change in W_A ¹⁹.

The chemical reactions occurring are probably similar to those described above for glass²². Supporting evidence that amino compounds are chemisorbed by metal oxide surfaces has recently been obtained by inelastic tunnelling spectroscopy²³. Further investigations are being carried out to find explanations for the differences observed in the effects of amine surface treatment of glass and of metal on the adhesion of this polyurethane to the substrate.

Acknowledgement

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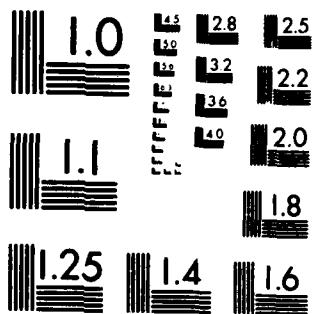
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